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Geometric polyhedral models for nanotubes comprising hexagonal lattices

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ABSTRACT

Two new models for the geometric structure of nanotubes comprising hexagonal lattices are described. The existing models for nanotubes typically involve rolled up planar sheets and ignore discrepancies due to curvature. The first of the models presented here assumes that all atomic locations are equidistant from the tube axis which applies for single species nanotubes such as carbon nanotubes. This model assumes that all bond angles and all bond lengths are equal in the cylindrical state, and that all atoms are equidistant from the tube axis, and from these three assumptions, expressions are given for the major geometric parameters. The second model extends this notion to tubes where all the atomic locations are not equidistant from the tube axis, which may be employed to model nanotubes comprising two chemical species that bond into a hexagonal lattice such as boron nitride nanotubes. In the second model, all bond lengths are taken to be equal and the atoms of the same species are taken to be equidistant from the tube axis, and the nanotube is assumed to comprise two species and thus there may be two radii. Fundamental to both models is the determination of a solution of a transcendental equation. Here we present a new formal Lagrange expansion of the solution. Previously given asymptotic series expansions of the exact formulae for both models lead to the conventional expressions as the leading order term. Although the correction terms are typically small, knowledge of the precise structure may be critical to comprehending many nanoscale phenomena. The new models also give rise to an expression for the wall thickness, an important geometric parameter for which at present no reliable information is available.

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1. Introduction

Since the well-publicised description of carbon nanotubes by Iijima [1], intensive research has been conducted into these structures and the literature now includes tens of thousands of articles dealing with various characteristics of nanotubes. In all but a handful of these articles [2–5], curvature effects are ignored and such carbon nanotubes are modelled as a planar sheet of graphene that has been simply rolled up into a right circular cylinder. The initial planar graphene state is assumed to comprise a network of perfectly regular hexagons, in the sense that all bond lengths and all bond angles are assumed to be identical. It is recognised that in the cylindrical state the bond lengths and bond angles are no longer equal in three-dimensional space, and it is generally considered that such variations are insignificant and may be ignored for most calculations.

The authors have recently developed a new polyhedral model for carbon nanotubes [6,7], which begins from the assumption that the hexagonal lattice should be perfectly symmetrical in the cylindrical state, and therefore postulates that all bond lengths and all bond angles are identical and moreover that all atoms are equidistant from the nanotube axis. These postulates give rise to a new geometric structure in which every atom is symmetrically equivalent to every other and

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that the covalent bonds in all directions are completely identical in length and angle. The new model gives rise to all the conventional formulae as the leading order terms of asymptotic expansions, but in addition they provide simple analytical correction terms to give the leading order effects of the curvature for such nanotubes. The polyhedral description also lends itself to a natural definition of thickness, which is fundamentally different from the thickness in a continuum sense, but which has yet to prove useful in mechanical models arising from the beam and elasticity theory, which are being applied to nanotubes.

While the correction terms are small, given the widespread interest and applications of carbon nanotubes, the knowledge of their precise geometric structure could be quite important to some applications. Furthermore, conceptualising carbon nanotubes as polyhedra, along with precise details of the geometric structure, may prove to be important in explaining some nanoscale phenomena, such as ultra-small nanotubes. Recently, a number of groups have been successful in producing very small radius carbon nanotubes in restricted environments, such as nanotubes with 2 Å radii which are formed in zeolite channels [8] and others with a radii of only 1.5 Å produced within the centre of multi-walled carbon nanotubes [9]. It has also been reported that these small nanotubes may possess novel properties [10], making them ideal components for new nano-electromechanical devices. High-curved nanotube like structures formed from sp^3 bonded carbon have also been suggested [11]. In all of these cases the nanotube radii involved are very small (2 Å or less) and in this range the curvature discrepancies inherent in the conventional rolled up model are not easily ignored.

The single species model described thus far may be extended to a two species model for which the atoms of each species are equidistant from the nanotube axis but different species may adopt different radii. An example of this type of structure is a boron nitride nanotube. Boron nitride nanotubes were first proposed by Rubio, et al. [12], and almost immediately numerical studies began to appear that investigate the properties of this potential new material [13]. The early studies concentrated on their electronic properties but more recently, articles have appeared which examine their mechanical properties [14]. More recent papers [15,16] examine their structural characteristics and in particular some authors have reported the precise structural dimensions of boron nitride nanotubes [17–19] based on numerical models. Using the detailed information from these *ab initio* investigations, the present authors extend the polyhedral model to encompass nanotubes comprising two chemical species [20], such as the structure found in boron nitride nanotubes. Fundamental to both models is a transcendental equation for which there is in general no known analytical solution, and the purpose of this paper is to present some new results for the Lagrange expansion of the solution of the transcendental equation.

In the following section we summarise the major results for the new polyhedral model for single species tubes and we give the known asymptotic expansions of the radius and thickness; the full details of which can be found in [6]. Thereafter, we give the major results from [20], which contains the new model for two species nanotubes such as boron nitride nanotubes. In Section 4 we present the new results for the transcendental equation, including the Lagrange expansion of the solution of that equation. In the final section of this paper we summarise the results and make some concluding remarks. We comment that at present there are a large number of well-defined molecular structures which might well be amenable to similar geometrical analysis. Here we assume that all these nanotubes are formed from a hexagonal framework of atoms. However, there are many other known molecules, often involving highly symmetrical geometrical configurations, for which a geometric analysis could prove to be profitable.

2. Single species model

For a single species nanotube comprising a hexagonal structure (e.g. carbon nanotubes) the conventional naming scheme [21] is adopted (n, m) where the chiral vector numbers n and m determine the arrangement of hexagons on the tube wall. In the conventional model the chiral vector numbers (n, m) prescribe a unique chiral vector $\mathbf{C}$ the length of which is given by

$$|\mathbf{C}| = \sigma\sqrt{3(n^2 + nm + m^2)}, \tag{1}$$

where σ is the bond length in the hexagonal lattice. The arrangement of hexagons around the nanotube wall is also characterised by the angle between the chiral vector and the vector applicable for zigzag nanotubes, that is nanotubes for which $m = 0$, which is termed the chiral angle and is given by

$$\cos\theta_0 = \frac{2n + m}{\sqrt{n^2 + nm + m^2}}.$$

From the chiral vector length (1), and by assuming that the nanotube is formed by rolling up the flat graphene sheet into a right circular cylinder in the direction of the chiral vector $\mathbf{C}$, we may immediately determine the radius, which is given by

$$r_0 = \sigma\sqrt{3(n^2 + nm + m^2)}/2\pi.$$

However, in making the assumption that the flat hexagonal sheet can be rolled into a right circular cylinder, we have implied that the covalent bonds in the lattice have become curved over the cylindrical surface. The effect of this assumption is to introduce asymmetrical distortions into the lattice structure which we assumed was symmetrical in the planar state. The primary purpose of the models described here is to determine a nanotube structure which is symmetrical in the cylindrical state, in the sense that all bond angles and bond lengths are equivalent, and thus the structure does not contain any of the distortions implied by a conceptual rolling up of a flat lattice.

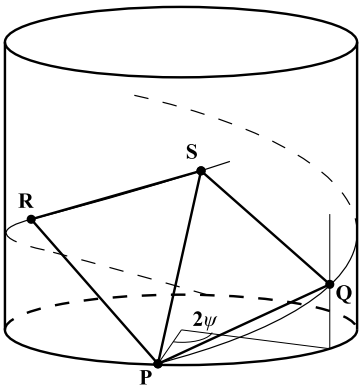

Fig. 1. Helices on the surface of a cylinder used to define the basic triangular lattice and the subtend, semi-angle ψ which they prescribe.

The model we develop is based on a polyhedral approach of covering a cylinder in such a way so as to ensure the symmetry of the nanotube structure. We begin by stating the postulates of this model which are as follows:

i. All bonds are of equal length.
ii. The angles between all adjacent bonds are equal.
iii. All atoms lie at an equal distance from the common tube axis.

From postulates (i) and (ii) it can be seen that if one takes a single atom from the nanotube and its three covalently bonded neighbours, then the overall structure must form an equilateral triangular pyramid with the central atom forming the apex of the pyramid and the three bonded atoms each forming one of the vertices comprising the base of the pyramid. Also, since the structure is symmetric, any of the atoms forming the base of this pyramid can also be considered the apex of a second pyramid where the base comprises its three covalently bonded atoms, which includes the atom located at the apex of the first pyramid, and this new pyramid is congruent to the first. Thus the approach adopted for the polyhedral model described here is to determine an arrangement of triangular pyramids which satisfies the three postulates given above.

The first step in developing this model is to determine an arrangement of triangles which cover the cylinder and satisfy the chiral arrangement (n, m) of the nanotube. This is done by first prescribing the angle subtended at the centre of the nanotube by a triangle edge in the plane perpendicular to the nanotube axis, we denote this angle 2ψ and call ψ the subtend semi-angle (see Fig. 1). From this definition we can prescribe helices $\alpha(t)$ and $\beta(t)$ on the cylindrical surface to be given by

$$\alpha(t) = (r\cos(2\psi t/m), r\sin(2\psi t/m), bt/m),$$
$$\beta(t) = (r\cos(2(\psi t - \pi)/m), r\sin(2(\psi t - \pi)/m), bt/m),$$

where r is the nanotube radius, b prescribes the pitch of the helix and t is a running parameter. We then define certain points lying on these helices to be given by $P = \alpha(0)$, $Q = \alpha(m)$, $R = \beta(n)$ and $S = \beta(n + m)$, such that the points PRS form an equilateral triangle. By imposing equidistant relations for the segments PQ, PR and PS we may derive the transcendental equation

$$(n^2 - m^2)\sin^2(\xi + \psi) - n(n + 2m)\sin^2\xi + m(2n + m)\sin^2\psi = 0, \tag{2}$$

where $\xi = (n\psi - \pi)/m$. We comment that in general there are few known analytical results for (2) and the formal Lagrange expansion of the solution is presented in Section 4. Eq. (2) may have many roots but we are interested in the roots that satisfy the inequalities

$$\pi/(n + m) \leqslant \psi \leqslant \pi/n,$$

which suffices to identify a unique root of (2) for any values of the chiral vector numbers (n, m). We also comment that while (2) is transcendental, simple solutions do exist for the special cases of zigzag tubes ($m = 0$) where $\psi = \pi/n$ and armchair tubes ($n = m$) where $\psi = \pi/2n$. However, there is in general no simple solution and typically the value of ψ is determined using a Newton–Raphson iterative scheme using the initial guess of $\psi_1 = \pi(2n + m)/[2(n^2 + nm + m^2)]$. We note that this approximation provides the exact values in the two special cases cited and arises at the leading order term from the Lagrange expansion of the transcendental equation, which we give later. Once the subtend semi-angle ψ is determined we may also determine the chiral angle θ, which is the angle between adjacent atoms lying on a single helix relative to the plane perpendicular to the nanotube axis. We find that the chiral angle θ is given by

$$\cos^2\theta = \frac{n(n + 2m)\sin^2\psi}{(n + m)^2\sin^2\psi - m^2\sin^2(\xi + \psi)}. \tag{3}$$

With the subtend semi-angle ψ and the chiral angle θ determined, the next step is to investigate how each pyramid is oriented in relation to the nanotube axis. To this end we begin with a pyramid which has some scaled height k which is then

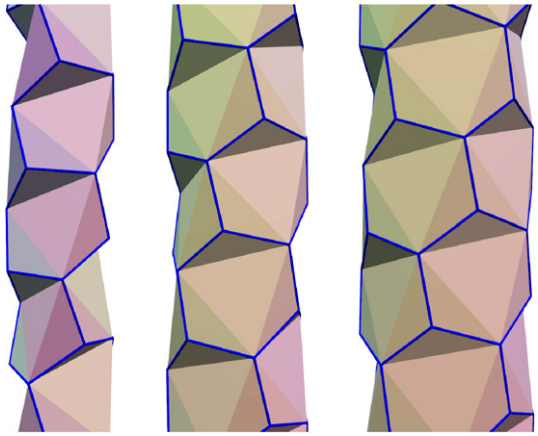

Fig. 2. (2, 1), (3, 1) and (4, 1) carbon nanotubes modelled with the polyhedral construction.

rotated so that the three points comprising the base of the pyramid lie at an equal distance from the nanotube axis and then the value of k is determined such that the apex of the pyramid is also at the same distance from the axis as the three vertices forming the base. To achieve this we must define another angle, which we call the slant angle ω and is given by

$$\sin\omega = \left(\sqrt{\cot^2\psi + 4\cos^2\theta - 3} - \cot\psi\right)/\sqrt{3}\cos\theta.$$

With the slant angle ω so determined, we may now derive a quadratic equation for the scaled pyramid height k, the solution of which is given by

$$k = (\sqrt{\mu^2 - 4\lambda\nu} - \mu)/2\lambda, \qquad \lambda = 1 - \sin^2\omega\cos^2\theta,$$
$$\mu = 2\cos\omega\cos\theta(\sin\omega\cos\theta + \sqrt{3}\cot\psi), \qquad \nu = 1 - \cos^2\theta(4 - \sin^2\omega) + 2\sqrt{3}\sin\omega\cos\theta\cot\psi,$$

and with k determined we may now also find the bond semi-angle ϕ which is found to be given by

$$\sin\phi = \sqrt{3/(4 + k^2)}.$$

At this point the construction is completely determined and the nanotube radius can now be given by

$$r = \sigma\sin\phi\cos\theta/\sin\psi.$$

We also comment that one important feature of the polyhedral model is that there arises a natural notion of tube thickness which can be defined as the difference between the inner and outer radii of the polyhedral structure. At this present point of time the physical significance of this definition is not clear. However, since it is a natural consequence of the model we give the formula for the thickness δ, which is given by

$$\delta = \sigma\sin\phi\cos\theta\tan(\psi/2).$$

Three particular nanotubes generated from this model are shown in Fig. 2

By a process of asymptotic expansions it is possible to determine the leading order and first order correction term of these parameters (for the full details see [6]) and from the expansions it is also possible to develop expressions in terms of the conventional parameters which capture the leading order effects of curvature. Two such expressions are for the radius r and thickness δ, which to leading order are given by

$$r = r_0 + \frac{\sigma^2(5 + \cos 6\theta_0)}{64 r_0} + O(1/n^3), \qquad \delta = \frac{3\sigma^2\cos^2\theta_0}{8 r_0} + O(1/n^3),$$

and we note that in both cases these expressions are accurate up to order $1/n^3$, and in developing these expressions we have assumed that $1/n \ll 1$, is a small parameter.

3. Two species model

The structure of nanotubes for a hexagonal lattice but comprising two atomic species is a little more complicated than the single species case because while we might expect that the atoms of one species to be positioned in a symmetrical arrangement, there is no reason to think that those locations will be equivalent for the second species. This has been confirmed by numerical studies (see for example [17–19]) for which distinct radii for the boron and nitrogen atoms are calculated for boron nitride nanotubes. Therefore, in the construction of this model we must accommodate the distinct characteristics of the two species, and specifically if one of the species undergoes the bending of its covalent bonds more

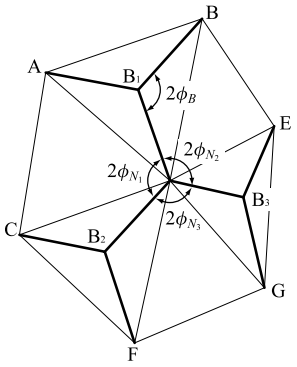

Fig. 3. Bond angles at the boron atoms ϕ_B and the three angles at the nitrogen atoms ϕ_{N_1}, ϕ_{N_2} and ϕ_{N_3}.

readily than those of the other species. In the case of boron nitride, it has been shown computationally [18] that the bond angles for nitrogen atoms are more readily distorted from the plane than is the case for the boron atoms.

The polyhedral model again begins with a set of postulates which extends the single species model presented in the previous section but at the same time accommodates the distinct nature of the two atomic species comprising the structure. The modified list of postulates for boron nitride nanotubes are as follows:

i. All bonds are of equal length.
ii. The angles between all adjacent bonds for the boron atoms are equal.
iii. All boron atoms lie at an equal distance from the common tube axis.
iv. All nitrogen atoms lie at an equal distance from the common tube axis.

We comment that postulate (ii) only applies to the boron atoms and in general the present model will lead to a structure with three distinct bond angles for the nitrogen atoms. However, to postulate that all bond angles are equal for the nitrogen atoms leads to the result that all bond angles for both boron and nitrogen are equal, which in turn leads to a structure where the boron and nitrogen atoms possess equal radii, which contradicts the findings of numerical studies. Thus, since the bond angles at the nitrogen atoms are found to be more readily bent, we assume that these bonds can adopt distinct angles but continue to impose the postulate (ii) for the bonds at the boron atoms. To characterise the degree to which the nitrogen atoms will bend compared with the boron atoms we include a fifth postulate which is:

v. There exists a fixed ratio of pyramidal height τ between the boron species, compared to the corresponding height in a symmetric single species nanotube.

This new parameter τ attempts to capture the difference in energetic cost to deform a bond angle at a boron atom as compared to the same deformation at a nitrogen atom. Thus in this construction we assume that the pyramids used to describe the polyhedral structure are arranged so that the boron atoms lie at the pyramid apices and the nitrogen atoms lie at the vertices that comprise the pyramid bases. Since the boron atoms are less readily bent, the pyramids for the boron nitride nanotube will be flatter than the corresponding pyramids in the single species model and therefore we assume that the value of τ lies between 0 and 1.

In this model we follow the same steps as outlined in the previous section. Specifically the subtend semi-angle ψ is given by (2) and the chiral angle θ is given by (3). However, when determining the bond semi-angle ϕ, we start to diverge from the previous model since now we have four bond angles. First is the bond semi-angle for the boron atoms ϕ_B, which is given by

$$\sin\phi_B = \sqrt{3/(4+\tau^2k^2)}.$$

There are no simple analytical expressions for the three bond semi-angles for the nitrogen atom ϕ_{N_1}, ϕ_{N_2} and ϕ_{N_3} (see Fig. 3). However, we may give approximate expressions which are determined from an asymptotic expansion of the implicit analytical expressions, which are

$$\sin\phi_{N_1} = \frac{\sqrt{3}}{2} - \frac{\sqrt{3}\pi^2[\tau^2(n^2+nm+m^2)+2(1-\tau)(n-m)^2]}{48(n^2+nm+m^2)^2} + O(1/n^4),$$

$$\sin\phi_{N_2} = \frac{\sqrt{3}}{2} - \frac{\sqrt{3}\pi^2[\tau^2(n^2+nm+m^2)+2(1-\tau)(n+2m)^2]}{48(n^2+nm+m^2)^2} + O(1/n^4),$$

$$\sin\phi_{N_3} = \frac{\sqrt{3}}{2} - \frac{\sqrt{3}\pi^2[\tau^2(n^2+nm+m^2)+2(1-\tau)(2n+m)^2]}{48(n^2+nm+m^2)^2} + O(1/n^4),$$

and these expressions are accurate up to order $1/n^4$, where we have assumed $1/n \ll 1$ is a small parameter.

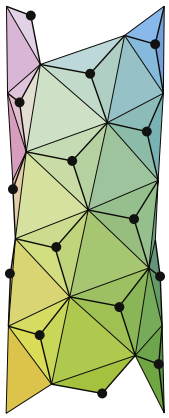

Fig. 4. (4, 2) boron nitride nanotube modelled with the polyhedral construction. The boron atoms are indicated with black dots and the nitrogen atoms are unmarked.

As previously mentioned, it has been calculated that boron nitride nanotubes possess two distinct radii, one for each atom species, and from the present model we may derive the following expression for the nitrogen radius

$$r_N = \sigma \sin\phi_B \cos\theta / \sin\psi .$$

The expression for the boron radius is more complicated but can be given as

$$r_B = \sigma \left[\sin^2\theta(\cos\omega - \tau k \sin\omega)^2 + \frac{(\tau k \cos\omega + \sin\omega + \sqrt{3}\cos\theta\cot\psi)^2}{4+\tau^2k^2} \right]^{1/2}.$$

Finally, we comment that if the two distinct radii r_B and r_N and the bond length σ are known, then the appropriate value of τ for that structure is given by the following approximate relation:

$$\tau \approx 1 - \frac{(r_N - r_B)(r_N + r_B)^2}{\sigma^2 r_N}.$$

A particular boron nitride nanotube generated from this model is shown in Fig. 4

4. New results for the transcendental equation Eq. (2)

We begin by deriving a curious antisymmetric relation from the transcendental equation Eq. (2), which may be rearranged to yield

$$n[n\sin^2(\xi+\psi) - (n+2m)\sin^2\xi] = m[m\sin^2(\xi+\psi) - (m+2n)\sin^2\psi].$$

We now define a new parameter $\chi(x, y) = \cos^{-1}\sqrt{x/2(x+y)}$, then after dividing by $2(n+m)$ the above equation may be expressed as

$$n[\cos^2\chi(n,m)\sin^2(\xi+\psi) - \sin^2\chi(n,m)\sin^2\xi] = m[\cos^2\chi(m,n)\sin^2(\xi+\psi) - \sin^2\chi(m,n)\sin^2\psi].$$

Now we introduce another new parameter $\gamma = n[\psi - \pi/(n+m)]$ so that

$$\psi = \frac{\gamma}{n} + \frac{\pi}{n+m}, \qquad \xi = \frac{\gamma}{m} - \frac{\pi}{n+m},$$

and thus the transcendental equation becomes

$$n\left[\cos^2\chi(n,m)\sin^2\left(\frac{\gamma}{n}+\frac{\gamma}{m}\right) - \sin^2\chi(n,m)\sin^2\left(\frac{\gamma}{m} - \frac{\pi}{n+m}\right)\right]$$
$$= m\left[\cos^2\chi(m,n)\sin^2\left(\frac{\gamma}{n}+\frac{\gamma}{m}\right) - \sin^2\chi(m,n)\sin^2\left(\frac{\gamma}{n} + \frac{\pi}{n+m}\right)\right].$$

Therefore, on defining the function $F(x, y, z)$ as

$$F(x,y,z) = x\left[\cos^2\chi(x,y)\sin^2\left(\frac{z}{x}+\frac{z}{y}\right) - \sin^2\chi(x,y)\sin^2\left(\frac{z}{y} - \frac{\pi}{x+y}\right)\right],$$

we may express the transcendental equation Eq. (2) in the compact form

$$F(n,m,\gamma) = F(m,n,-\gamma), \tag{4}$$

where the antisymmetry of the relationship is now clear.

Table 1
Comparison of radii from conventional model, new model and *ab initio* calculations of [23] using $\sigma = 1.44$ Å.

nanotube	r_0 (Å)	r (Å)	[23] (Å)
(4, 0)	1.59	1.71	1.71
(3, 2)	1.73	1.81	1.8
(4, 1)	1.82	1.92	1.91
(5, 0)	1.98	2.08	2.06
(3, 3)	2.06	2.13	2.12
(4, 2)	2.10	2.17	2.17
(5, 1)	2.21	2.29	2.28
(6, 0)	2.38	2.46	2.45
(4, 3)	2.41	2.47	2.46

The next result for the transcendental equation is an expansion for the root of interest of (2) using the method of Lagrange expansions. We begin by expanding the compound angle in (2) to give

$$(n^2 - m^2)(\sin^2\xi\cos^2\psi + 2\sin\xi\cos\xi\sin\psi\cos\psi + \cos^2\xi\sin^2\psi) - n(n+2m)\sin^2\xi + m(2n+m)\sin^2\psi = 0,$$

and now dividing through by $\cos^2\xi\cos^2\psi$ yields

$$(n^2 - m^2)(\tan^2\xi + 2\tan\xi\tan\psi + \tan^2\psi) - n(n+2m)\tan^2\xi\sec^2\psi + m(2n+m)\tan^2\psi\sec^2\xi = 0.$$

On replacing $\sec^2 x = 1 + \tan^2 x$, where $x \in \{\psi, \xi\}$ and collecting like terms of $\tan\xi$ gives

$$[(n^2 - m^2)\tan^2\psi + m(2n+m)]\tan^2\xi - 2(n^2 - m^2)\tan\psi\tan\xi - n(n+2m)\tan^2\psi = 0,$$

which is a quadratic expression in $\tan\xi$. From geometrical considerations we wish to have $\tan\xi < 0 < \tan\psi$ and which means that we specifically require the negative square root term of the solution of the quadratic equation and therefore we may write

$$\xi = -\tan^{-1}\left(\frac{\sqrt{(n^2+nm+m^2)^2 + n(n+2m)(n^2-m^2)\tan^2\psi} - (n^2-m^2)}{(n^2-m^2)\tan\psi + m(2n+m)\cot\psi}\right).$$

However, we recall that $\xi = (n\psi - \pi)/m$, and therefore the transcendental Eq. (2) is equivalent to

$$\pi = n\psi + m\tan^{-1}\left(\frac{\sqrt{(n^2+nm+m^2)^2 + n(n+2m)(n^2-m^2)\tan^2\psi} - (n^2-m^2)}{(n^2-m^2)\tan\psi + m(2n+m)\cot\psi}\right).$$

With reference to "Lagrange's theorem" as detailed in [22, Section 7.32] we define a function $f(\Psi)$ by

$$f(\Psi) = n\Psi + m\tan^{-1}\left(\frac{\sqrt{(n^2+nm+m^2)^2 + n(n+2m)(n^2-m^2)\tan^2\Psi} - (n^2-m^2)}{(n^2-m^2)\tan\Psi + m(2n+m)\cot\Psi}\right),$$

and we require the value of $\Psi = \psi$, for which $f(\psi) = \pi$. The Lagrange expansion for this root is given by

$$\psi = \sum_{k=1}^{\infty}\frac{\pi^k}{k!}\left\{\frac{\mathrm{d}^{k-1}}{\mathrm{d}\Psi^{k-1}}\left[\frac{\Psi}{f(\Psi)}\right]^k\right\}_{\Psi=0}, \tag{5}$$

where we comment that this expression has been simplified by noting that $f(0) = 0$.

5. Results

We now present the predictions of the new model compared with those of the rolled up model. In Fig. 5 we plot the relative difference between the radius prediction from the rolled up model r_0 and that of the polyhedral model. We see that there is a general trend of larger relative difference as the nanotubes become smaller which is explained by the increased curvature in this regime. Furthermore, we note that zigzag tubes are more greatly affected by the curvature than are chiral tubes, and armchair tubes exhibit the smallest difference in the predictions of the two models. In Table 1 we show the radii predicted by the conventional rolled up model r_0, the radii predicted by the polyhedral model r and those radii reported by Cabria, et al. [23] using *ab initio* calculations. As can been seen from this table, the polyhedral model is in excellent agreement with the *ab initio* calculations, and eventhough they differ slightly at the third significant digit, the trend of variation is consistent over the range of tube sizes. This is in contrast to the conventional formula which displays reasonable agreement for large tubes but very little agreement for the nanotubes possessing small radii and therefore does not exhibit the same trend as apparent from the polyhedral model and the results in [23].

Finally, in this section we compare the asymptotic expressions given in [6] with the results that emerge from evaluating terms in series (5). We denote the kth term of the series from (5) by ψ_k and we find that all the even terms vanish and thus

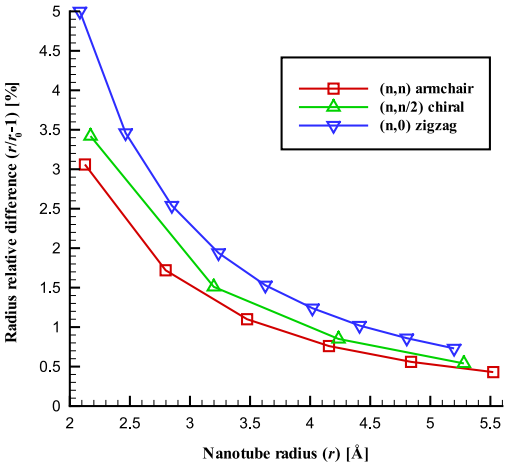

Fig. 5. Relative difference between the polyhedral and rolled up model prediction for tube radius for carbon nanotubes of type zigzag: (5, 0)–(13, 0), chiral: (4, 2)–(10, 5), and armchair: (3, 3)–(8, 8).

we have

$$\psi = \sum_{j=0}^{\infty} \psi_{2j+1},$$

where, after some algebra, the first ten nonzero terms are given by

$$\psi_1 = \frac{\pi(2n+m)}{\Delta},$$

$$\psi_3 = \frac{\pi^3 \Omega \Lambda}{\Delta^5},$$

$$\psi_5 = -\frac{\pi^5 \Omega \Lambda(\Delta^3 - 60\Omega^2)}{15\Delta^9},$$

$$\psi_7 = \frac{\pi^7 \Omega \Lambda[11\Delta^6 - 84\Omega^2(23\Delta^3 - 330\Omega^2)]}{1260\Delta^{13}},$$

$$\psi_9 = \frac{\pi^9 \Omega \Lambda\{\Delta^9 + 2\Omega^2[239\Delta^6 - 210\Omega^2(53\Delta^3 - 420\Omega^2)]\}}{1260\Delta^{17}},$$

$$\psi_{11} = \frac{\pi^{11} \Omega \Lambda(233\Delta^{12} - 18\Omega^2\{3844\Delta^9 - 33\Omega^2[16613\Delta^6 - 2380\Omega^2(157\Delta^3 - 855\Omega^2)]\})}{1247400\Delta^{21}},$$

$$\psi_{13} = \frac{\pi^{13} \Omega \Lambda[1819\Delta^{15} + 3\Omega^2(116393\Delta^{12} - 1092\Omega^2\{35369\Delta^9 - 330\Omega^2[5399\Delta^6 - 105\Omega^2(733\Delta^3 - 3036\Omega^2)]\})]}{48648600\Delta^{25}},$$

$$\psi_{15} = \frac{\pi^{15} \Omega \Lambda \left\{ \begin{array}{c} 103289\Delta^{18} - 4\Omega^2[1420051\Delta^{15} - 12\Omega^2(153358931\Delta^{12} \\ -1638\Omega^2\{9495648\Delta^9 - 385\Omega^2[704179\Delta^6 - 6900\Omega^2(1051\Delta^3 - 3510\Omega^2)]\})] \end{array} \right\}}{13621608000\Delta^{29}},$$

$$\psi_{17} = \frac{\pi^{17} \Omega \Lambda \left(\begin{array}{c} 1067429\Delta^{21} + 6\Omega^2\{8080961\Delta^{18} - 6\Omega^2[1824528547\Delta^{15} - 102\Omega^2(3558681809\Delta^{12}) \\ -30030\Omega^2\{6092557\Delta^9 - 1950\Omega^2[60623\Delta^6 - 3654\Omega^2(133\Delta^3 - 372\Omega^2)]\})] \end{array} \right)}{694702008000\Delta^{33}},$$

$$\psi_{19} = \frac{\pi^{19} \Omega \Lambda \left[\begin{array}{c} 73976863\Delta^{24} + 24\Omega^2 \left(56239174\Delta^{21} + 3\Omega^2\{44805119951\Delta^{18} \right. \\ -1596\Omega^2[10551041033\Delta^{15} - 204\Omega^2(4551492301\Delta^{12} \\ \left. -2730\Omega^2\{54595048\Delta^9 - 4785\Omega^2[165689\Delta^6 - 10230\Omega^2(106\Delta^3 - 255\Omega^2)]\})]\}\right) \end{array} \right]}{237588086736000\Delta^{37}},$$

where $\Delta = 2(n^2 + nm + m^2)$, $\Omega = 3nm(n+m)$, $\Lambda = m(2n+m)(n+2m)(n-m)$ and we comment that ψ_2, ψ_4, ψ_6, etc., all vanish, such that $\psi_{2k} = 0$, for $k \in \{1, 2, 3, \ldots\}$. We also note that ψ_1 and ψ_3 reproduce the expansion given in [6, eqn (12)], where they are determined by the method of asymptotic expansions. However the expressions for ψ_5, ψ_7, ψ_9, etc., up to ψ_{19} are determined from the Lagrange expansion (5), and have not previously appeared in the literature. The structure given here represents a nontrivial reformulation of these basic expressions and although this structure is not well understood by the authors, nevertheless the given explicit formulae constitute a major simplification. As can be seen from Fig. 6, the convergence to the exact numerical values can be readily obtained only for a few terms for small values of the principle chiral vector number n and convergence improves for larger values of n.

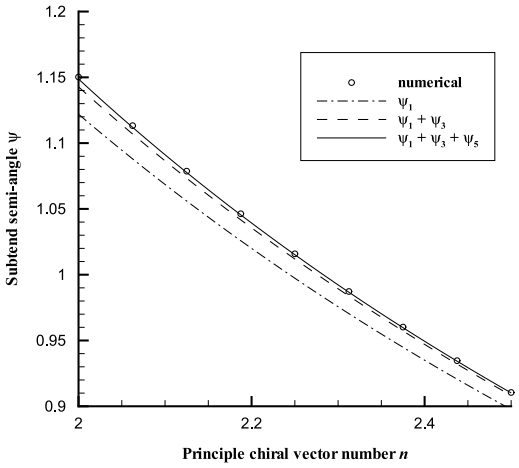

Fig. 6. Numerically computed values of subtend semi-angle ψ for nanotubes with chirality $(n, n/2)$.

6. Conclusions

In this paper we present an overview of the polyhedral models for nanotubes which have been applied to nanotubes comprising single and double chemical species. Fundamental to both models is the transcendental Eq. (2) for which we have produced two new results. Firstly, we manipulate the equation into an antisymmetric form (4) which may be of use in the future analysis of this equation. Secondly, we deduce a Lagrange expansion for the parameter ψ, Eq. (5), which provides a formal mechanism to generate an expansion for ψ which is equivalent to that which is produced by asymptotic expansion. We also give the first ten nonzero terms from this expansion which show that the first two terms do indeed coincide with the asymptotic expansion given in [6] and the next seven nontrivial terms are published here for the first time.

The particular models emphasise the importance of geometric issues in molecular configurations. Particular molecular structures are formulated on the basis of minimum energy, and it happens that the minimum energy configurations are frequently those which possess a high degree of symmetry. We have demonstrated that a purely geometric analysis of such structures may yield important information on critical parameters, such as the radius of the nanotube. From a mathematical discipline perspective, much remains to be done in terms of geometric analysis of accepted molecular structures.

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